A Heterojunction Carbon Solar Cell "Au/a-C:H(N)/p-Si/Au"

D.K.Mishra[1], T.Soga[2], Maheshwar .Sharon[3]*

[1]Dept. of Chemistry, IIT Bombay, Powai, Mumbai-400076, India

[2]Environ. Tech. and Urban Planning, NIT, Showa-ku, Gokiso-cho, Nagoya, Japan

[3]Walchnad Center for Research in Nanotechnology and Bionanotechnology, Walchand College of Arts and Science, Solapur, Maharashtra, 413 006, India

Abstract: **Carbon thin film from mixture of carbon soot of camphor and urea is prepared by pulsed laser ablation technique. Urea is used as a nitrogen source. Carbon film is characterized by EPMA, XPS, ESR and Raman. The Current-Voltage characteristic of a heterojunction cell "Au/a-C:H(N)/p-Si/Au" is studied under AM1.5 conditions. The maximum solar to electrical efficiency of 1.08% is observed from carbon thin film ablated at 200°C and maximum quantum efficiency is found to be 41.6% at 600nm, whereas carbon films prepared at 500°C though shows lower quantum efficiency (~15%) but it gives almost same efficiency with light of wavelength from 600 nm to 950nm.**

Keywords: **Nitrogen doped carbon, Urea as a source of N_2, Carbon solar cell, Pulse laser deposition, Quantum efficiency Vs temperature**

I. INTRODUCTION

Since the discovery of diamond like carbon in 1971 [1], there have been a lot of efforts made to use the amorphous carbon for various applications. Mayerson and Smith [2] explained the possibilities of doping of amorphous carbon and since then many efforts are made to prepare doped carbon thin film for various applications. After the pioneer work of Veeraswamy et al.[3], which opened a new dimension of application of amorphous carbon, there has been many publications dealing with the various application of amorphous carbon e.g., carbon solar cell [4-6]. Most of the reports are focused on either making a device from carbon films or microstructural studies of the carbon film, but little discussion has been made towards the bonding structure with specific device application such as carbon solar cell. In this article we report about doping of carbon film using urea (as a source of nitrogen) by pulsed laser deposition to make a heterojunction carbon solar cell of configuration "Au/a-C:H(N)/p-Si/Au" and examine the influence of microstructure on solar cell characteristics.

II. EXPERIMENTAL

An excimer laser of wavelength 308 nm (XeCl) was used for the laser ablation and deposition of carbon thin film from the soot of carbon.. Target as a pellet was prepared from a mixture of powder of carbon soot (generated by burning camphor) and urea 5wt% (as a source of nitrogen). Details of this method is discussed elsewhere [7]. P-type Silicon wafer (for making a heterojunction solar cell) and quartz plate (for characterization purposes) were cleaned with acetone/methanol in ultrasonic bath and then etched with HF (1:10 HF and water) before putting inside the stainless steel deposition chamber. After getting the vacuum of order 10^{-5} torr, the deposition of carbon films was done by using 4800 laser shots with a repetition rate of 10 Hz having fluence $2*10^8 W/cm^2$ per pulse. The films were deposited at two substrate temperatures i.e. 200°C and 500°C. Carbon films deposited on quarts plate were used for microstructural characterization of the carbon thin film. Carbon film deposited on p-Si was used for making a solar cell of configuration "Au/a-C:H(N)/p-Si/Au". Thin film of Au was deposited by vacuum evaporation for making ohmic contact.

III. RESULTS AND DISCUSSION

The thickness of the films was measured by stylus method and found to be 175±5 nm and 125±5 nm for film deposited at substrate temperature of 200°C and 500°C respectively. The growth rate of carbon film found to be 0.36nm/sec and 0.26nm/sec films deposited at 200°C and 500°C respectively. It is rather surprising to observe that thickness of film and the deposition rate of carbon film was low for deposition temperature of 500°C. Perhaps at higher temperature before carbon film could adhered to the substrate, it was getting evaporated due to high vacuum in the chamber. Data of the transmittance and reflectance were used to calculate the band gap of carbon film using the Tauc plot of $\{(\alpha h\nu)^{1/2}$ Vs h\nu\}. For this α was assumed to approximately same as the OD obtained from the absorption plot. From the intercept of linear graph on the hv axis when $(\alpha h\nu)^{1/2} = 0$ the optical band gap found to be 0.9 eV and 0.6eV for films prepared at substrate temperature of 200°C and 500°C respectively. The lower optical gap observed could be due to the size of aromatic ring clusters which is inversely proportional to optical gap.

Elemental analysis by EPMA revealed the presence of nitrogen as 3.003at% and 2.47at % for the carbon film prepared at 200°C and 500°C respectively. Low at % of nitrogen with film prepared at 500°C may be because nitrogen

from urea might not have chance to favorably interact with carbon soot under high vacuum condition. Surface composition and nature of bonding in the film was analyzed by XPS. Peaks appeared around 283eV and 400.5 eV corresponds to carbon (Figure 1A & B) and nitrogen (inset of Figure 1, film prepared at 200^0C) respectively.
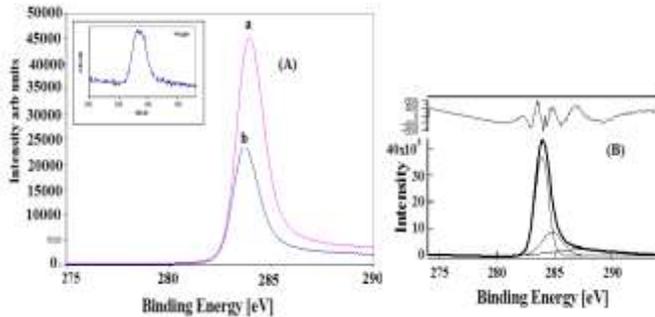

Figure 1 (A) XPS spectra of carbon film prepared at substrate temperature of (a) 200^0C and (b) 500^0C, showing the peak around 283.5.0 eV for C1s. The inset showing the peak of Nitrogen 1s around 400.4eV, for the film prepared at 200^0C and (B) .Deconvolution of carbon 1s peak, film prepared at 200^0C

Lower at % of nitrogen (1.09 at%) with film prepared at 200^oC obtained with XPS as compared to EMPA analysis maybe because the former analysis gives the results of surface while EPMA gives the total amount of nitrogen present in the film. [8]. The deconvolution of Carbon 1s peak (Figure 1B) produced three peaks centered at 283.9eV, 284.8eV and 287.6eV. The first two peaks are assigned as sp^2 bonded carbon (88.7%) and sp^3 bonded carbon (9.7%) respectively. The third peak at 287.6eV could be due to C-N or C-O bonding present in the film. The Nitrogen 1s peak position (400.5eV) is matching with the reported one [9]. The nitrogen-carbon could be associated with a ring (aromatic) or a chain structure (aliphatic) inside the carbon matrix.

The ESR (JES FE1XG ESR spectrometer) measurements were carried out at liquid nitrogen temperature (77 K) using 100 kHz field modulation, a microwave frequency of about 9.263 GHz, and the microwave power of 0.4 mW. A typical ESR plot (intensity Vs magnetic field) is shown in the Figure 2 and the peak around 3300
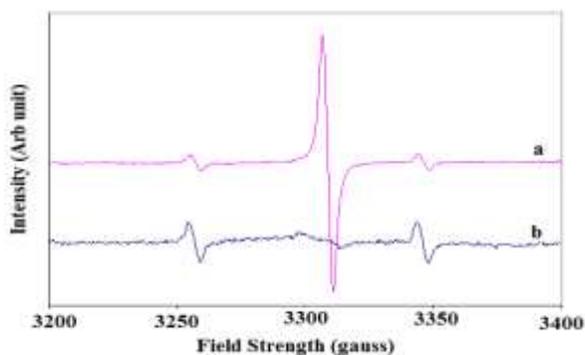

Figure 2: ESR spectra of carbon film doped with nitrogen deposited at substrate temperature of (a) 200^0C and (b) 500^0C

Gauss corresponds to carbon whereas the other two belongs to Mn^{2+} which is used as the reference. ESR spectra indicated a higher spin density for nitrogen doped carbon films i.e. $1.52*10^{19}$ and $1.63*10^{20}$ cm^{-3} with g-value of 2.0058 and 2.0041 respectively for the film obtained at 500^0C and 200^0C. The higher g-value than free electron (2.0023) indicates presence of two different paramagnetic centers associated in the films. The dissimilar g-value could be due to the presence of heteroatoms (nitrogen or oxygen) around the carbon in different bonding environments. But the ESR g factor is less useful for a-C because carbon has a low atomic number and small spin orbit coupling so most defects lie at g =2.0028. Also, there is no hyperfine information because ^{12}C is a spin zero nucleus. Thus ESR line width gives information about the kind of defects present in the film. The peak-to-peak line width increases [10] when deposition temperature increases from 200 to 500^0C (ΔHpp= 4.0 to 9.0) because the lattice vibrations reduce the spin mobility by scattering effects [11]. The increase in line width could be due to oxygen association with the film [12]. It is also seen that with increase of optical band gap the ΔHpp decreases, which is supported by others [13]. On the contrary the spin density is decreased with the increase of substrate deposition temperature as reported by Watanabe et al.[14]. This variation may be due to difference in nitrogen amount present in the film. From the spin density values it is clear that amorphous carbon film prepared at 200^0C contained higher spin ($1.63*10^{20}$ cm^{-3}). This could be due to presence of nitrogen atom (i.e. in ring or chain structure [15]).

Raman spectra of nitrogen doped carbon films were taken using an NRS-2000 (NEC) instrument. An Ar-laser having 514.5 nm wavelengths at 20 mW power with a spot size of 4 μm was used to observe the spectra after the acquisition time of 300s. Two bands appeared in our films and there is a shift in the D-band towards higher wave number, and the G-band peak remained more or less near to ~1560cm^{-1} (In amorphous carbon films generally two broad bands observed [16,17] at ~1360 cm^{-1} and ~1560 cm^{-1} named D-band (disorder/defect band) and G-band (graphitic band) respectively). To be precise, the G-peak appeared at 1545.2 cm^{-1} and 1561.0 cm^{-1} for the film prepared at 200^0C and 500^0C respectively (Figure 3).
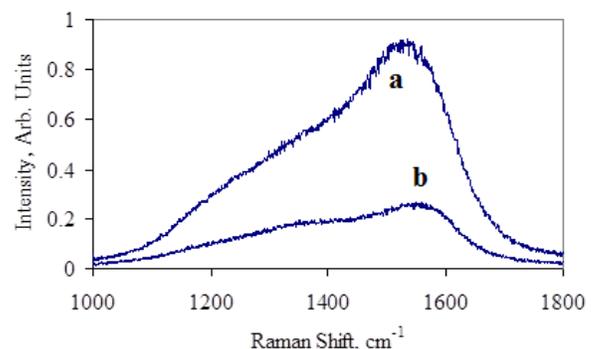
Figure 3: Micro-Raman spectra of carbon film prepared at substrate temperature of (a) 200^{0}C and (b) 500^{0}C

The G peak position towards that of graphite (1580cm^{-1}) suggests an increase in amount of sp^2 bonding or there may be ordering within the sp^2 carbons. But XPS results of the carbon films does not support the increase of sp^2 bonding. Hence there must be ordering of sp^2 carbon in the film prepared at 500^{0}C, that is why reduction in optical gap. By examining the peak positions of carbon films prepared at 200^{0}C and 500^{0}C it can be said that the film prepared at lower substrate temperature contains more chain (olefinic) structure than the film prepared at higher temperature. This is because of more downward shift in G-position from the graphitic value (G-peak =1580 cm^{-1}). It was found that the presence of nitrogen in the film encouraged Carbon sp^2 bonding[18] which is explained by the quantitative XPS analysis for films prepared at two substrate temperature of 500^{0}C and 200^{0}C (~ 85.8% and 88.7% respectively). The I$_D$/I$_G$ of both the films were measured and found that film prepared at higher temperature is having higher value (1.27) as compared to the film prepared at lower temperature (1.07). The higher I$_D$/I$_G$ value indicated that there is an increase in the number of sp^3 configured carbon atoms than with film prepared at 200°C [19]. Presence of sp^3 carbon atoms will make the film more resistive than film containing sp^2 carbon atom. This is also supported by the result of series resistance of the film. The film prepared at 500°C showed higher resistance (327.8 Ω) as compared to film prepared at 200°C (13.3 Ω).

A heterojunction photovoltaic cell of configuration "Au/a-C:H(N)/p-Si/Au" was prepared using the nitrogen doped carbon film grown at 200^{0}C and 500°C substrate temperature. The current-voltage (I-V) characteristics of this device showed moderate rectification with a conversion efficiency of 1.08%. The Voc and Isc were obtained to be 0.26V and 11.79mA/cm^2 respectively (Figure 4) for film prepared at 200°C. When the substrate temperature increased to 500^{0}C the solar cell parameters were decreased drastically as shown in the inset of figure 4 (Voc = 0.15, Isc = 0.098, ff = 0.24 and Eff = 0.0035).

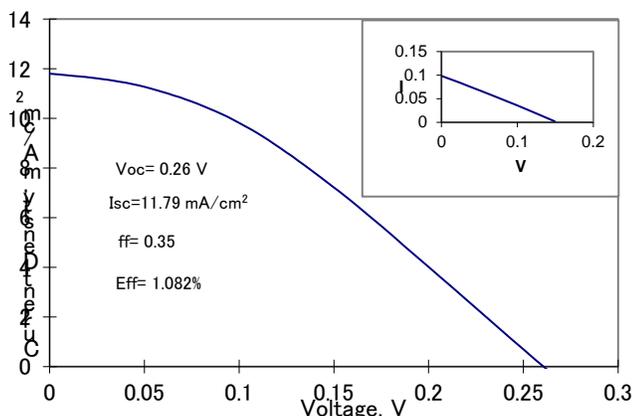Figure 4: Current density-Voltage characteristics of a-C:H(N)/p-Si heterojunction in dark as well as under simulated light, 100mW/cm^2. The

inset shows the plot of the film prepared at 500^{0}C.

The lower solar cell efficiency may be due to (a) absence of nitrogen on the surface, which corresponds to the absence of true doping and (b) the higher series resistance (327.8 Ω for the film prepared at 500^{0}C as compared to 13.3 Ω for 200^{0}C). (c) Since thickness of films (175±5 nm and 125±5 nm for films deposited at 200°C and 500°C respectively) deposited at 200oC was more than for film deposited at 500°C suggesting a shorter depletion width with film prepared at 500°C and hence lower solar conversion efficiency and (d) nitrogen doping was also higher for film deposited at 200°C than the film deposited at 500°C which might be responsible for giving lower resistance for film deposited at 200°C and hence low solar efficiency for film of 500°C. Due this reason photocurrent for film deposited at 200°C was more as compared to film deposited at 500°C. Variation of quantum efficiency with wavelength of incident light shows two broad peaks centered at 600 nm and 950 nm (Figure 5) corresponds to carbon and silicon respectively as reported in literature [3].
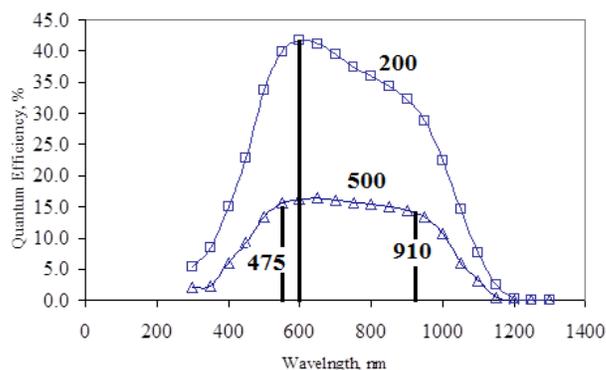

Figure 5: Quantum efficiency of the heterostructure, a-C:H(N)/p-Si solar cell, under zero bias and constant photon density of 1*10^{14}/cm^2. The a-C:H(N) film prepared at substrate temperature of 200^{0}C (Δ) and 500^{0}C (Δ)

The quantum efficiency found to be more and distinct for the film prepared at 200^{0}C as compared to the film of 500^{0}C perhaps because film prepared 200°C shows well established quantum efficiency at a very specific wavelength of light (600nm) while film prepare at 500°C though shows a broader quantum efficiency for light from 600nm to 950nm, but its quantum efficiency is only around 15% due to higher resistance of the film and lower depletion width.. The influence of p-Si on overall efficiency cannot be ruled out as there may be some percentage of light reach the surface of p-Si. The influence of local microstructures around carbon (presence of nitrogen) is also playing a major role in the performance of the device. The maximum efficiency of nitrogen doped carbon film having maximum spin density supports that in graphitic carbon the paramagnetic states (spin density) are not the dominant recombination centers and do not limit the efficiency [20]. In this regard more exhaustive studies are required to find out why (i) growth rate of film prepared at 500°C is low (ii) the band gap is also low for film deposited at 500°C and the role of depletion region width.

IV. CONCLUSIONS

In conclusion, thin films of carbon deposited by pulse laser using a mixture of soot of camphor as a natural source and urea as a source of nitrogen are used to fabricate a photovoltaic solar cell of configuration Au-C:H(N)/p-Si/Au. The XPS study confirmed the true doping of nitrogen in the carbon film. The higher spin density (10^{20}/cm^3) of nitrogen doped carbon film is found not to degrade the efficiency, in fact nitrogen doping helped it effectively.

ACKNOWLEDGEMENTS

REFERENCES

[1]. S.Aisenberg and R.Chabot, J. App. Phys., 42 (1971) 2953
[2]. B.Meyerson, and F.W.Smith, Solid State Communication, 34, (1980) 531
[3]. V.S.Veerasamy, J.Yuan, G.A.J.Amaratunga, W.I.Milne, K.W.R.Gilkes, M.Weiler, and L.M.Brown, Phys. Rev. B, 48, (1993) 17954
[4]. H.A.Yu, T.Kaneko, S.Yoshimura, Y.Suhng, and S.Otani, App. Phy. Lett., 69 (1996) 4078
[5]. K.M.Krishna, M.Umeno, Y.Nukaya, T.Soga and T.Jimbo, Appl. Phys. Lett. 77, (2000) 1472
[6]. Xuemin Tian, Tetsuo Soga, Takashi Jimbo and Masayoshi Umeno, Journal of Non-Crystalline Solids 336 (2004) 32
[7]. S.M.Mominuzzaman, K.M.Krishna, T. Soga, T. Jimbo and M.Umeno, Jpn. J. Appl. Phys. 38, (1999) 658
[8]. N.Hellgren, M.P.Johansson, E.Broitman, L.Hultman and J.E.Sundgren, Phys. Rev. B 59, (1999) 5162
[9]. Y. Hayashi, K.M. Krishna, H. Ebisu, T. Soga, M. Umeno and T. Jimbo, Diamond and Relat. Mater. 10, (2001) 1002
[10]. G. Fanchini, S.C. Ray, A. Tagliaferro and E. Laurenti, Diamond and Relat. Mater. 11, (2002) 1143
[11]. F. Demichelis, C. DeMartino, A. Tagliaferro and M. Fanciulli, Diamond and Relat. Mater. 3, (1994) 844
[12]. M. Hoinkis, E. D. Tober, R. L. White and M. S. Crowder, Appl. Phys. Lett. 61, (1992) 2653
[13]. K. M. Krishna, H. Ebisu, K. Hagimoto, Y. Hayashi, T. Soga, T. Jimbo, and M. Umeno, Appl. Phys. Lett. 78, (2001) 294
[14]. I.Watanabe, S.Hasegawa and Y.Kurata, Jpn. J. Appl. Phys., 25, (1982) 856
[15]. [J.Robertson and C.A.Davis, Diamond and Relat. Mater. 4, (1995) 441
[16]. R.Kalish,, Y.Lifshitz, K.Nugent and S.Prawer, Appl. Phys. Lett., 74, (1999) 2936
[17]. A. C.Ferrari and J.Robertson, *Phys. Rev. B*, 61, (2000) 14095
[18]. N.V.Sidgwick, The organic chemistry of Nitrogen, 2nd Edition, Oxford University Press, Oxford, 1937
[19]. N.M.J. Conway, A.C. Ferrari, A.J. Flewitt, J. Robertson, W.I. Milne, A. Tagliaferro and W. Beyer, Diamond and Relat. Mater., 9, (2000) 765
[20]. Susanne Schutte, Stephan Will, Helmut Mell and Walther Fuhs, Diamond and Relat. Mater., 2, (1993) 1360